



Performance of zinc molybdenum phosphate in anticorrosive paints by accelerated and electrochemical tests

B. DEL AMO, R. ROMAGNOLI* and V.F. VETERE

CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIC–CONICET), Calle 52 e/121 y 122, (1900) La Plata, Argentina

(*author for correspondence, e-mail: cidepint@ba.net)

Received 9 July 1998; accepted in revised form 11 May 1999

Key words: accelerated tests, coatings, corrosion, phosphate pigments, zinc molybdenum phosphate

Abstract

This work studied the anticorrosive behaviour of micronized ‘zinc molybdenum phosphate’ (zinc phosphate modified with zinc molybdate). It was proposed to evaluate its efficiency in solvent borne paints with 30 and 15% of the pigment by volume and a pigment volume concentration/critical pigment volume concentration ratio (PVC/CPVC) of 0.8. The behaviour of paints formulated with different binders such as epoxy, chlorinated rubber, vinyl and alkyd resins, was assessed by accelerated (salt spray cabinet and accelerated weathering) and electrochemical tests. Epoxy and chlorinated rubber paints showed the best anticorrosive performance. The inhibitive action of ‘zinc molybdenum phosphate’ was confirmed. Good correlation was obtained between salt spray and electrochemical tests.

1. Introduction

Organic coatings are effective in protecting steel in corrosive environments. Traditional anticorrosive paints contain lead or hexavalent chromium compounds as active pigments. The use of classical red lead and zinc chromates is being restricted by increasing environmental awareness and stringent national and international regulations. These pigments contaminate the environment and represent a risk to human health, particularly during the production process and paint removal operations.

The long awaited reduction in the employment of classic active pigments has induced a search for suitable alternative products over more than 15 years. Particular attention has been paid to zinc phosphate whose effectiveness can be improved by modifying the particle size distribution or its chemical composition with suitable elements such as molybdenum, aluminium etc. Other pigments have also been developed by substituting orthophosphate by polyphosphate anions.

The protective action of zinc phosphate results from phosphating the metal substrate along with the formation of complex substances with binder components [1, 2]. More recent studies confirmed the presence of an oxyhydroxide film on the steel surface [3–5]. The protection mechanism is also assumed to arise from the polarization of cathodic areas by the precipitation of sparingly soluble salts, such as phosphates, on the metal substrate [5, 6]. The low solubility of zinc phosphate and

the fact that this pigment is a coarse crystalline precipitate also hinder the growth of effective anticorrosive films [7, 8].

The behaviour of coatings pigmented with zinc phosphate in accelerated tests led to disappointing results; however, these paints showed a good performance in outdoor long exposure tests [8, 9–14]. Recent investigations claim that the protective properties of zinc chromate cannot be achieved by zinc phosphate [8, 9] except for the special case of alkyd paints [15]. As a consequence, a second generation of modified zinc phosphate pigments was developed [8–10].

‘Zinc molybdenum phosphate’ belongs to the so called second generation phosphate pigments. It is prepared from zinc phosphate added with zinc molybdate expressed as MoO_3 , up to 1%. This pigment is claimed to have equal or superior anticorrosive behaviour than chromates and better than zinc phosphate on its own [1, 2, 8, 9]. The active inhibitive species of the pigment is the molybdate anion which repassivates corrosion pits in steel [16]. Little information is available in the literature about its anticorrosive performance. Adrian and Bittner [8, 9] reported the behaviour of zinc molybdenum phosphate in alkyd paints showing that this pigment can perform as well as zinc chromate and better than zinc phosphate. Zinc molybdenum phosphate and other pigments of the second generation were also tested in compliant primers with promising results [9, 17].

The purpose of the present research is to report the anticorrosive properties of zinc molybdenum phosphate

in solvent-borne paints. Four binders were used: epoxy, chlorinated rubber, vinyl and alkyd resins. Two pigment contents, 30 and 15% v/v, were employed to formulate the paints. The ratio pigment volume concentration/critical pigment volume concentration (PVC/CPVC) was 0.8 for all tested paints. Anticorrosive behaviour was evaluated by accelerated and electrochemical tests. This work is a follow up to previous research about the use of zinc phosphate in paints with different binders [15].

2. Experimental details

2.1. Paints composition and manufacture

The binders employed in this research were as follows: bisphenol A epoxy resin/polyamide (1/1 v/v), chlorinated rubber 10 cP/chlorinated paraffin 42% (70/30 w/w), vinyl resin (91% vinyl chloride, 3% vinyl acetate, 5.7% alcohols)/tricresyl phosphate (4/1 w/w) and a medium oil alkyd (50% linseed and tung oils, 30% *o*-phthalic anhydride, 8% pentaerythritol and glycerol and 12% pentaerythritol resinate).

The solvent mixture employed for epoxy paints was toluene/methyl isobutyl ketone/butyl alcohol (36/52/12% w/w); for chlorinated rubber paints xylene/Solvento 100 (4/1 ratio w/w) was used; for vinyl resin the solvent mixture was 'Cellosolve acetate'/methyl isobutyl ketone/xylene (70/10/20% w/w); while white spirit was used for alkyd paints. Solvent borne paints were chosen to evaluate pigment performance because their behaviour has been well documented for many years.

Micronized zinc molybdenum phosphate was employed as anticorrosive pigment in two different contents, 30 and 15% v/v, respectively. Titanium dioxide, talc and barium sulphate were also incorporated to complete the pigment formula. The PVC/CPVC relationship was 0.8. Composition of tested paints is shown in Table 1.

Paint manufacture was carried out employing a ball mill with a 3.3 l jar. Pigments were dispersed in the vehicle for 24 h to achieve an acceptable dispersion degree.

Paints were applied by means of a spray gun on SAE 1010 steel panels (15.0 cm × 7.5 cm × 0.2 cm) up to a thickness of $75 \pm 5 \mu\text{m}$. The composition of SAE 1010 steel is as follows: C: 0.12%, Si: 0.01%, Mn: 0.35%, S: 0.02% and P: 0.02%. Tested panels were previously sandblasted to Sa 2 1/2 (SIS 05 59 00, $20 \pm 4 \mu\text{m}$ maximum roughness), followed by degreasing with toluene. A second series of panels was prepared by topcoating primed specimens with an alkyd paint up to a dry film thickness of $40 \pm 5 \mu\text{m}$. The composition of the topcoat, expressed as v/v, was as follows: titanium dioxide, 7.3%; alkyd resin, 20.8%; chlorinated rubber (R10), 44.8%; 42% chlorinated paraffin, 2.1% and solvents 65%.

Painted panels were kept indoors for seven days before being tested.

2.2. Laboratory tests

2.2.1. Salt spray test (ASTM B 117)

A scratch line was made through the coating with a sharp instrument so as to expose the underlying metal to the aggressive environment. The panels were evaluated to establish the rusting degree (ASTM D 610) and to assess failure at the scratch mark (ASTM D 1654) after 650 and 1300 h exposure, respectively. In all cases tests were carried out in triplicate by determining the mean value of the obtained results.

2.2.2. Accelerated weathering (ASTM G 26)

The accelerated degradation of painted samples was carried out in an Atlas Weather-o-meter (Xenon arc). The test program consisted of a 102 min light cycle followed by a 18 min light and water spray cycle, therefore, the overall time of each cycle was 2 h. The cycling was continued up to 720 h. Blister formation, degree of rusting and failure at the scratch marks were evaluated according to the above mentioned standards.

2.2.3. Corrosion potential measurements

The electrochemical cells were constructed by delimiting 3 cm² circular zones on the painted surface. An acrylic tube, 7 cm high, with one flat end was placed on the specimen and filled with the electrolyte (0.5 M sodium

Table 1. Percentage solids in paint composition (by volume)

Paints	1	2	3	4	5	6	7	8
Zinc molybdenum phosphate	5.8	11.6	5.8	11.6	5.8	11.6	5.8	11.6
Titanium dioxide	5.6	4.8	5.6	4.8	5.6	4.8	5.6	4.8
Talc	13.8	11.3	13.8	11.3	13.8	11.3	13.8	11.3
Barium sulphate	13.8	11.3	13.8	11.3	13.8	11.3	13.8	11.3
Epoxy resin/polyamide resin (1/1 ratio)	61.0	61.0	—	—	—	—	—	—
Chlorinated rubber/chlorinated paraffin (70/30 ratio)	—	—	61.0	61.0	—	—	—	—
Vinyl resin/tricresyl phosphate (4/1 ratio)	—	—	—	—	61.0	61.0	—	—
Medium oil alkyd	—	—	—	—	—	—	61.0	61.0

Note: The solvent mixture employed for epoxy paints was toluene/methyl isobutyl ketone/butyl alcohol (36/52/12, wt %); for chlorinated rubber paints was xylene/Solvento 100 (4/1 ratio by weight); for vinyl resin was 'Cellosolve acetate'/methyl isobutyl ketone/xylene (70/10/20, wt %) while white spirit was used for alkyd paints

perchlorate solution). Corrosion potential of coated steel was measured employing a calomel electrode as reference and a high impedance voltmeter.

2.2.4. Ionic resistance measurements

The resistance between the coated steel substrate and a platinum electrode was also measured employing the cells described previously and an ATI Orion, model 170, conductivity meter at 1000 Hz. Similar determinations were performed on uncoated steel.

2.2.5. Polarization resistance measurements

The polarization resistance of painted specimens was determined as a function of immersion time by employing the described cell with three electrodes. The reference electrode was calomel and the counterelectrode a platinum grid. The sweep amplitude was ± 10 mV, starting from the corrosion potential at a scan rate of 0.166 mV s^{-1} . Measurements were taken employing a model 272A EG&G PAR potentiostat/galvanostat plus Softcorr 352 software. Polarization resistance of uncoated steel was also monitored as a function of immersion time.

3. Results and discussion

3.1. Salt spray test (ASTM B 117)

The results obtained in the salt spray cabinet after 650 and 1300 h of testing are shown in Tables 2 and 3, respectively. Blistering was not observed on any of the tested paints. For both pigment contents, the epoxy resin was found to provide the most efficient anticorrosive protection. A similar behaviour was observed for paints formulated with chlorinated rubber.

Anticorrosive behaviour of topcoated panels was observed to improve notably after 1300 h exposure without significant signs of corrosion except for systems containing paints 7 and 8. Corrosion products of nonaggressive type were detected after removing the paint from the panels coated with vinyl and alkyd paints pigmented with 15% of zinc molybdenum phosphate. The improved behaviour was due to an in-

Table 3. Rusting degree (ASTM D 610) and failure at the scratch mark (ASTM D 1654) after 650 and 1300 h exposure in the salt fog chamber for steel panels covered with the anticorrosive paint plus a topcoat

Paint	Rusting		Failure at the scratch mark	
	650 h	1300 h	650 h	1300 h
1	10	10	10	10
2	10	10	10	10
3	9	9	9	9
4	10	10	10	10
5	9	8	9	7
6	10	10	8	8
7	8	6	7	6
8	9	7	6	5

creased barrier effect obtained by topcoating the primed panels.

The anticorrosive behaviour of epoxy and chlorinated rubber paints was found to improve with respect to that of paints formulated with zinc phosphate. Thus, to achieve a similar performance, the paint pigmented with zinc phosphate needed a $40 \mu\text{m}$ thickness topcoat and in the case of chlorinated rubber binder 0.03% of the surface showed signs of corrosion in spite of being topcoated [18].

Vinyl paints containing zinc molybdenum phosphate showed an extended life with respect to those containing zinc phosphate. Thus, to reach a given corrosion degree, paints containing zinc molybdenum phosphate took 650 h of exposure; whereas, paints pigmented with zinc phosphate took only 400 h [19]. A similar behaviour was observed with the alkyd binder [18].

When comparison is made among paints formulated with zinc chromate and the less resistant resins (vinyl and alkyd), vinyl paints pigmented with zinc chromate deteriorated after 96 h of exposure developing oxide spots on the painted surface [19]. Substitution by zinc molybdenum phosphate resulted in clear protective advantages. Nonsignificant differences in performance were observed between alkyd paints pigmented either with zinc chromate or with zinc molybdenum phosphate [15].

Undercutting rusting was similar for paints containing zinc phosphate and for paints pigmented with zinc molybdenum phosphate. Better results were obtained with the alkyd binder when phosphate pigments were employed instead of zinc chromate [15, 19].

3.2. Accelerated weathering (ASTM G 26)

All paints exhibited a good behaviour after 720 h exposure in that no blister or significant signs of corrosion were observed on the panels. Topcoating of panels enhanced the system barrier properties, therefore improving the behaviour of vinyl and alkyd systems (Table 4). It is expected that these paint systems would perform acceptably in outdoor exposures for at least two years without showing signs of corrosion. This

Table 2. Rusting degree (ASTM D 610) and failure at the scratch mark (ASTM D 1654) after 650 and 1300 h exposure in the salt fog chamber for steel panels covered with the anticorrosive paints

Paint	Rusting		Failure at the scratch mark	
	650 h	1300 h	650 h	1300 h
1	8	8	9	9
2	10	10	10	10
3	9	9	8	7
4	10	10	9	8
5	8	7	7	6
6	6	5	6	5
7	6	5	6	5
8	7	6	8	7

Table 4. Rusting degree (ASTM D 610) and failure at the scratch mark (ASTM D 1654) after 360 and 720 h exposure in the Weather-o-meter for steel panels covered with the anticorrosive paint plus a topcoat

Paint	Rusting		Failure at the scratch mark	
	360 h	720 h	360 h	720 h
1	10	10	10	10
2	10	10	10	10
3	10	10	10	10
4	10	10	10	10
5	10	9	10	9
6	10	10	10	10
7	10	8	10	8
8	10	9	10	9

Note: None of the samples presented blistering

expectation is based on the literature report which established that 700 h of accelerated weathering are equivalent to two years outdoor exposure.

3.3. Corrosion potential measurements (Figure 1)

The corrosion potentials of panels coated with paints formulated with epoxy and chlorinated rubber resins (30% zinc molybdenum phosphate) were observed to shift positively as time elapsed with a slightly decay after 25 and 50 days of immersion, respectively (Figure 1(a)). For paints made with chlorinated rubber, the corrosion potential was observed to increase again after 40 days of immersion due to the sealing of small pores by corrosion products. At the same time that oxide spots were observed on the surface, the shape of the polarization curve became linear due to an ohmic control. The shifting of the corrosion potential of epoxy coated panels, during the test period, could also be due to pigment–binder interaction. This topic will be the subject of further studies. After analysing the four paints, chlorinated and epoxy coating showed the best anticorrosive performance in the salt spray test. These results were further confirmed by measurements of the corrosion potential.

The corrosion potential of panels covered with paints formulated with alkyd and vinyl resins were found to shift towards more positive values, during the first 24 h of immersion; the reference being the corrosion potential of bare steel in 0.5 M sodium perchlorate solution. After this time, the corrosion potential was observed to change quickly to more negative values because of the increasing number of conductive paths through the paint film and the attending incoming of the electrolyte solution (Figure 1(a)). After a few days these paints attained the final value, about +150 mV with respect to the corrosion potential of bare steel.

The corrosion potential of painted steel was observed to change with the corroded area. However, it never reached the bare steel corrosion potential because a fractional area of test specimen remained undamaged, that is free from blisters and corrosion spots (100% for

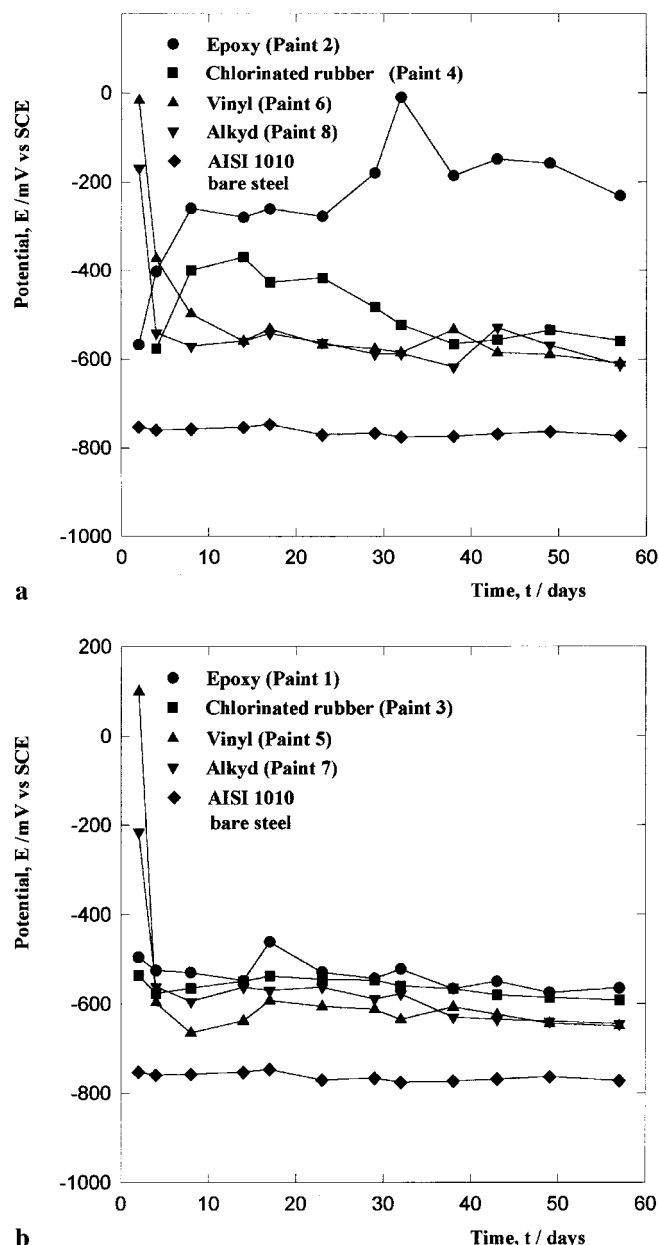


Fig. 1. Corrosion potential of painted steel panels as a function of the exposure time in 0.5 M sodium perchlorate solution. Zinc molybdenum phosphate pigment: (a) 30% and (b) 15%.

epoxy, 99% for chlorinated rubber paint, 94% for vinyl and 40% for alkyd paints). Moreover, a fraction of the attacked area remain in the passive state at the end of the test.

In all cases studied in this research, the shifting of the corrosion potential to more noble values was due to the low film permeability and to the presence of zinc molybdate in the coating. Mo(VI) compounds are supposed to constitute the passive layer together with phosphates [20]. Ambrose et al. [16] found that molybdenum compounds are effective in increasing the re-passivation rate in crevices and pits.

On the one hand, a lower content of zinc molybdenum phosphate, down to 15%, was observed to impair the anticorrosive protection since the corrosion potential

shifted towards more negative values with immersion time. On the other hand, epoxy paints still showed good anticorrosive performance for the same percentage. No significant changes were detected among panels covered with paints formulated with alkyd and vinyl resins which rapidly acquired the final corrosion potential (Figure 1(b)).

3.4. Ionic resistance measurements (Figure 2)

The measured resistance is composed of two contributions: the solution and the paint film resistance. When the solution resistance is low, about $84\ \Omega$, the paint film resistance is responsible for the measured values. Polarization effects may be neglected at the measuring frequency employed in this test (1 kHz). The initial values for the ionic resistance decreased as follows (Figure 2(a) and (b)): $R_{\text{paint 4}} > R_{\text{paint 6}} > R_{\text{paint 2}} > R_{\text{paint 8}} > R_{\text{paint 3 and 5}} > R_{\text{paint 1}} > R_{\text{paint 7}}$.

The values of the resistance at the initial stage are of crucial importance because they are used to predict the coating useful life [21]. All paints studied (pigment content 30%) give rise to films with high initial resistance ($> 10^6\ \Omega\ \text{cm}^{-2}$), enough to protect steel by a barrier effect (Figure 2(a)). Full protection was achieved when the ionic resistance exceeded $10^8\ \Omega\ \text{cm}^{-2}$ [21]; in this sense, chlorinated rubber and vinyl paints exhibited the highest initial barrier effect. However, as time progressed, chlorinated rubber and epoxy coatings proved to be the most resistant to water and ion penetration, therefore ensuring a very good performance for both paints during the immersion period.

Although paints with chlorinated rubber showed the highest resistance values at the beginning of the test, a higher tendency to pinholing was detected as compared with epoxy paints. Pore sealing by corrosion products in chlorinated rubber paints after 40 days of immersion was noticed by a slight increment of the resistance at the end of the immersion period. During the test period, the resistance of epoxy paints was observed to slowly decrease and, at the same time, no iron oxide spots were observed neither on the paint film nor under it.

Significant changes of the ionic resistance during the first days of immersion were observed for vinyl and alkyd paints. These results reflect an increasing permeability to the electrolyte solution through macropores which extended to the base metal. The corrosion potential was found to reach its final average value when the ionic resistance fell in the 10^4 – $10^5\ \Omega\ \text{cm}^{-2}$ range. This stage was accompanied by total electrolyte penetration through the coating and, eventually, blister formation [21].

The initial resistance was found to decrease, on average, by two orders of magnitude when the pigment content was lowered from 30 to 15%. Thus, the initial barrier effect disappeared in the case of vinyl and alkyd paints while in the other cases the effect was only attenuated (Figure 2(b)).

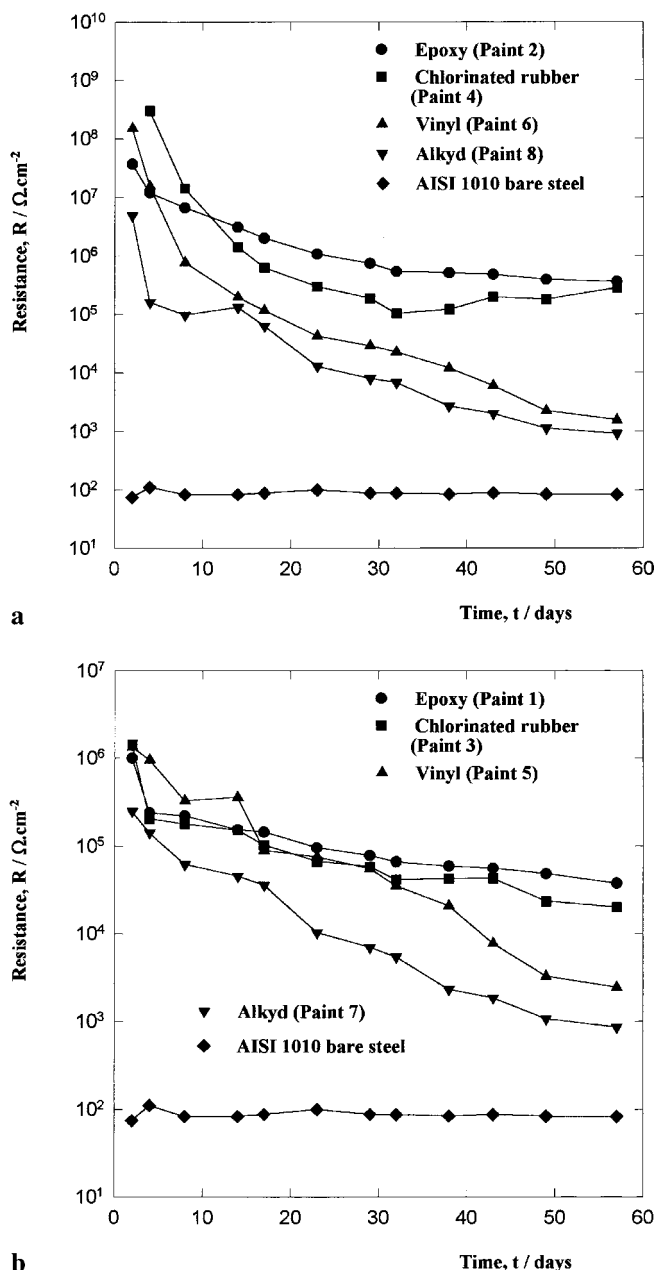


Fig. 2. Ionic resistance of painted steel as a function of the exposure time in 0.5 M sodium perchlorate solution. Zinc molybdenum phosphate pigment: (a) 30% and (b) 15%.

3.5. Polarization resistance measurements (Figure 3)

Polarization resistance, as measured in this work includes the ionic resistance. As a general rule, it may be observed that it is higher than the ionic resistance, confirming that the tested pigment has inhibitive properties [21], in agreement with previous results where zinc phosphate (the main component of zinc molybdenum phosphate) reduced the corrosion rate of iron [5]. Furthermore, molybdenum compounds were shown to increase the steel polarisation resistance therefore improving the corrosion resistant of the substrate, even in the presence of chlorides. The addition of molybdenum hexavalent anions were reported to decrease the critical

current density for passivation and increase the stability of passive films [16].

Panels painted with chlorinated rubber and epoxy paints (30% of zinc molybdenum phosphate) showed the highest polarization resistance values while vinyl and alkyd paints showed an important decrease of this magnitude with the immersion time (Figure 3(a)).

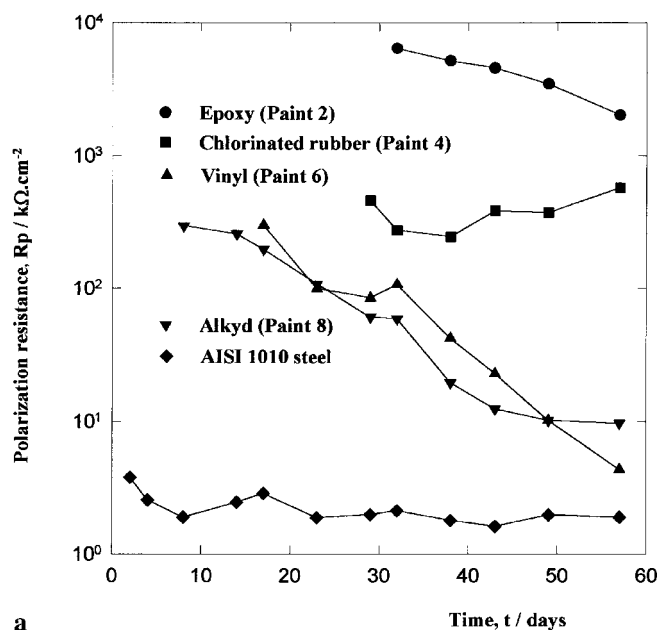
The action of molybdenum compounds is particularly significant in the case of vinyl and alkyd binders. Thus, paints formulated with these binders were observed to have low ionic resistant values and the polarization resistance resulted higher than the ionic counterpart, therefore indicating that the protection was provided only by the inhibitive action of the pigment. By contrast,

in the case of chlorinated rubber and epoxy paints the protective properties of the paint were linked to the barrier effect.

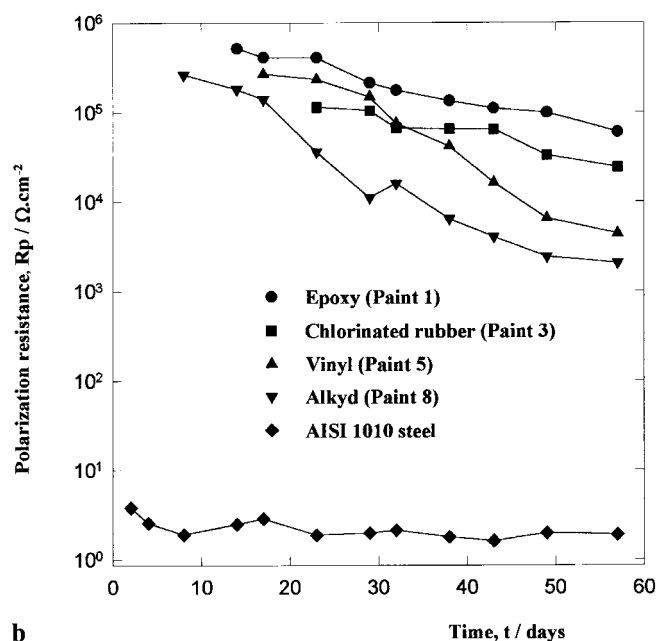
The polarization resistance of alkyd paints may be ten times higher than the ionic resistance. This may be attributed not only to the inhibitive action of the pigment but also to the high reactivity of this binder with the substrate and the pigment. The corrosion inhibition of steel by the formation of soap was known from early times [1, 2]. As a result, alkyd paints presented less ferric oxide spots at the end of the test than what could be expected from the low resistance values registered during it. However, some blisters were formed, but underneath the metal surface remained oxide free.

When the pigment content was diminished at 15%, the protection afforded by the anticorrosive paint was poorer (Figure 3(b)).

The pigment inhibitive action is due to the precipitation of a ferric phosphate layer on the metal surface; loose ferric phosphate seals the film pores. Ferrous phosphate may be formed at previous stage along with iron oxides which precipitated on the metal surface [22]. Scanning electron microscopy (SEM) analysis performed on oxide spots revealed the presence of amorphous



a



b

Fig. 3. Polarization resistance of painted steel panels as a function of the exposure time in 0.5 M sodium perchlorate solution. Zinc molybdenum phosphate pigment: (a) 30% and (b) 15%.

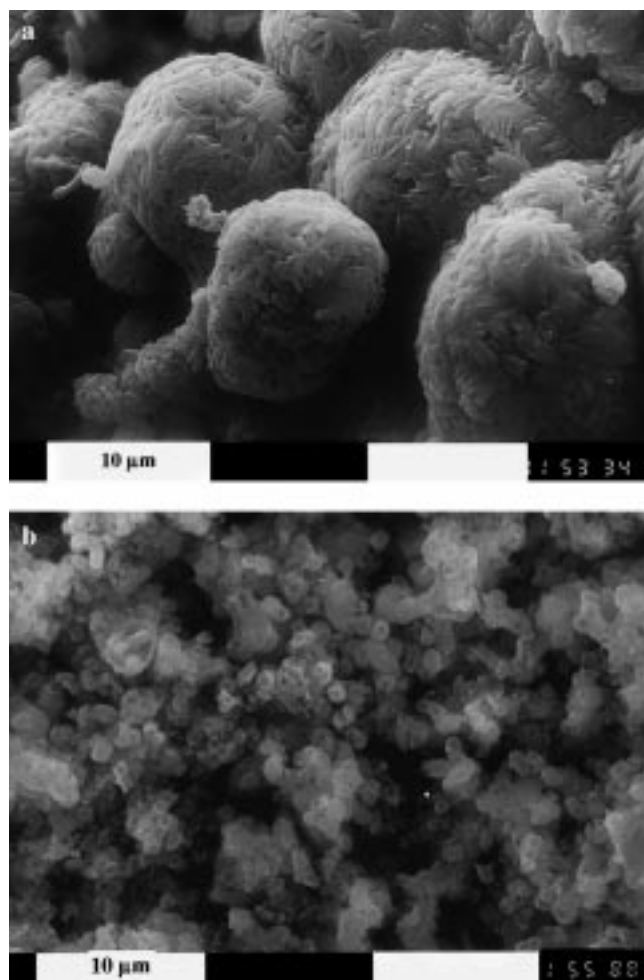


Fig. 4. SEM micrographs of (a) globular iron oxide formations, (b) indented globular iron oxide partially stabilized by the precipitation of ferric phosphate (3100×).

iron oxide and some globular formations resembling lepidocrocite nests. These structures are supposed to form more stable oxide morphologies in the sense that they have a fine structure constituted by sticks shaped particles (Figure 4(a)). The transformation from globular to stick like structures has been thought to be induced by the presence of some elements such as Al, Mg, Si, Ti and Zn, coming from the pigments in the paint film [23]. Ferric phosphate was observed around the oxide spots where the surface concentration of P was 3–11% and that of Fe 97–89% (Figure 4(b)). Regions rich in phosphorous were observed as indented spherical particles.

4. Conclusions

The following can now be stated:

- (i) Paints formulated with epoxy and chlorinated rubber resins, with a zinc molybdenum phosphate content as low as 15% v/v with respect to the total amount of pigments, showed a good anticorrosive performance. However, a 30% content is recommended to obtain the best performance for each type of binder.
- (ii) The inhibitive properties of zinc molybdenum phosphate were reflected in the high value of the polarization resistance as compared with the ionic counterpart.
- (iii) Confirming the efficiency of the total paint system applied on steel, all samples showed a good behaviour in the Weather-o-meter test after 720 h exposure.
- (iv) Good correlation was found between salt spray and electrochemical tests.

Acknowledgements

The authors are grateful to CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and CIC

(Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) for their sponsorship. The authors also wish to thank Colores Hispania, providers of the anticorrosive pigment.

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